

Low Temperature CO Oxidation on the Pt(111) Surface

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Abstract: *In situ* X-ray methods were used to characterize the oxidation of CO on Pt(111) in the temperature range where molecular oxygen dissociates. Temperature Programmed Fluorescence Yield Near Edge Spectroscopy (TP-FYNES) experiments, capable of monitoring reactions under reactive atmospheres, were performed in pressures up to 0.01 Torr. These experiments were used to characterize this reaction over an extended pressure range (UHV to 0.01 Torr) for the first time. Studies of CO with coadsorbed molecular oxygen indicate repulsive interactions between the two adsorbates. Only when oxygen is forced to adsorb in the proximity of coadsorbed CO will oxidation occur at 140 K. Under UHV conditions, oxygen must be adsorbed prior to CO in order for carbon dioxide to form at 140 K. However, when heated in increasing pressures in oxygen, preadsorbed partial monolayers of CO will react with oxygen to form carbon dioxide at 140 K (**Figure 1**). These results suggest repulsive interactions between molecular oxygen and CO on Pt(111) and only when oxygen is forced to adsorb in the vicinity of CO will reaction occur at 140 K. Isothermal experiments of preadsorbed partial CO monolayers yield an activation energy of 4.3 kJ/mol (**Figure 2**). The reaction does not go to completion under these conditions, even when held at the reaction temperature with a huge excess of oxygen, suggesting a self-limiting mechanism.

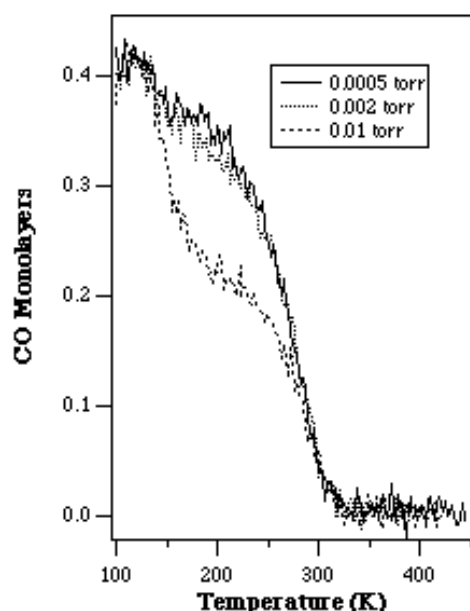


Figure 1. TP-FYNES of preadsorbed partial ML CO heated in three oxygen pressures at 287.8 eV. The low temperature oxidation channel is driven by increasing oxygen pressures.

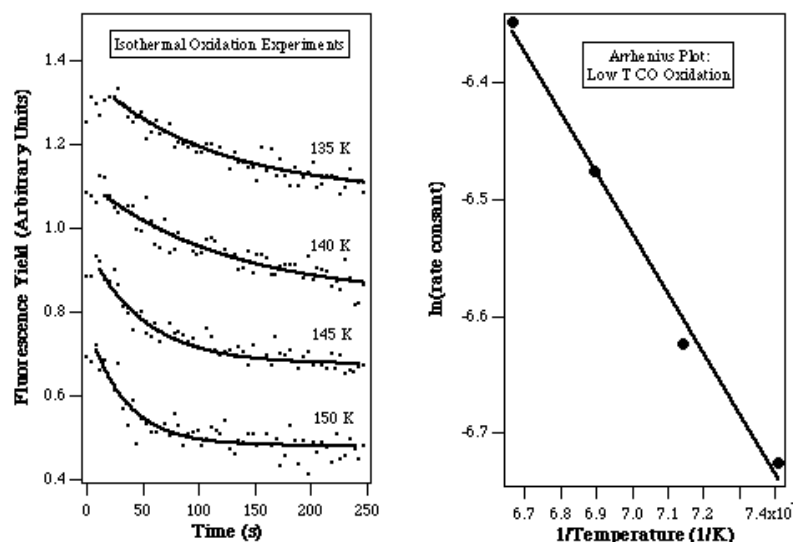


Figure 2. Isothermal kinetic experiments (left panel) of partial ML CO near the low temperature reaction zone (135 to 150 K) under 0.01 Torr of oxygen. Arrhenius plot (right panel) of low temperature CO oxidation, yielding an activation energy of 4.3 kJ/mol.